Today

I. Note unusual homework due date/time
II. Last Time
III. Statistical Mechanics
IV. Binary Model Example

I. We proved that entropy is a `state function'. Other examples of state variables are temperature and pressure.

These are variables that don't depend on how you got to where you are in the state space.

It's also useful to contrast these with non-state variables, or path dependent variables, such as heat and work.

We've also been discussing reversible and irreversible processes.

I. In a reversible process:

$$\Delta S_{\text{tot}} = 0$$

How is a reversible process even possible? In a reversible proces, heat goes into the system and comes out of the environment at the same T, so

$$\Delta S_{\text{system}} = -\Delta S_{\text{environment}}.$$

Irreversible process: process can only go one way:

$$\Delta S_{\text{tot}} > 0.$$

II. Statistical mechanics is the study of systems with many particles. Let's introduce some terminology:

Microstate: a description of every particle.

Macrostate: characterized by thermodynamic variables ($N, V, P, T, U, S, \ldots$).

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Multiplicity (of a macrostate):

$\Omega =$ number of microstates corresponding to a given macrostate.

3 coins. I tell you that there are two heads (specifies the macrostate), then what is the multiplicity?

HHT (an example microstate)

HTH

THH

$\Omega = 3$.

3 coins with two or more tails. What is the Ω? (TTH, THT, HTT, TTT), then $\Omega = 4$.

II. You are dealt a hand of 5 cards from a deck that consists of only the numbers 1-5, and only the suits H and D.

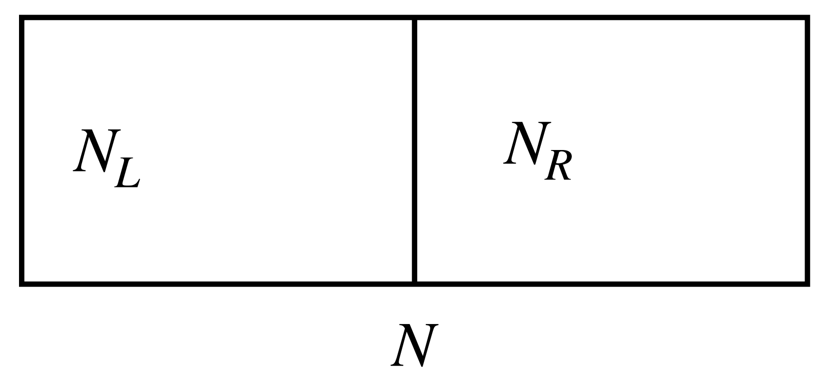
You have a hand that consists of a straight, meaning you have the numbers 1-5 and you have three diamonds in your hand. What's the multiplicity?

1D2D3D4H5H, 1H2D3H4D5D
1D2D3H4D5H, 1H2H3D4D5D
1D2H3D4D5H, $\Omega = 10$.
1H2D3D4D5H
1D2D3H4H5D
1D2H3D4H5D
1H2D3D4H5D
1D2H3H4D5D

II. Entropy: $S = k \ln \Omega$. (where k is Boltzmann's constant).
Unit is J/K.

Let's study an example of this way of getting the entropy of the system.

III. Let's consider a binary model. What is the number of ways that I can put N molecules into this box?



Microstate: a particular assignment of the molecules—2^N ways to do this.
Macrostate: specification of both N and N_L, the number on the left side of the box. (it follows that $N_R = N - N_L$)
Multiplicity: $\Omega(N, N_L)$ a count of all microstates consistent with the specification of N and N_L.

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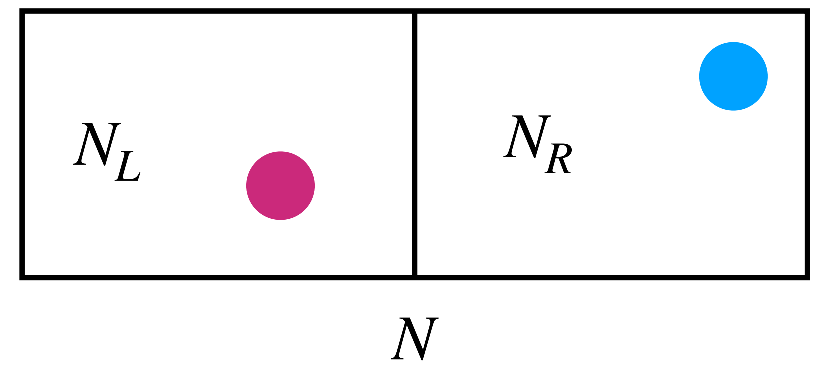

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To figure this out, let's do some special cases

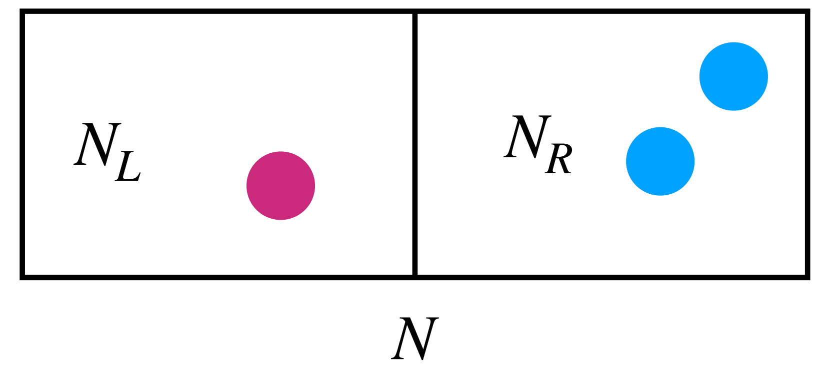
$\Omega(1,1) = 1$, $\Omega(1,0) = 1$,

$\Omega(2,2) = 1$, $\Omega(2,1) = 2$, $\Omega(2,0) = 1$

$\Omega(3,3) = 1$, $\Omega(3,2) = 3$, $\Omega(3,1) = 3$, $\Omega(3,0) = 1$

III. When we put the particles out on a line we get $N!$ permutations of them.

We next select N_L particles to put on the left side of the box.



$$\Omega(N, N_L) = \frac{N!}{N_L!N_R!} = \frac{N!}{N_L!(N - N_L)!} \equiv \binom{N}{N_L}$$

$$\binom{5}{2} = \frac{5!}{2!3!} = \frac{5 \cdot 4}{2 \cdot 1} = 10.$$

$10^{23}!$ is so big that we can't really deal with it analytically.

<u>Suppose:</u> N is large, and the "imbalance" s is a small fraction of N

$N_L = \dfrac{N}{2} + s$, or more precisely $\dfrac{2s}{N} \equiv x \ll 1.$

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We'll be using Stirling's approximation:

$$N! \approx \sqrt{2\pi N}\, e^{-N} N^N.$$